

Phase Equilibria Diagrams

Phase Diagrams for Ceramists

Volume XI Oxides

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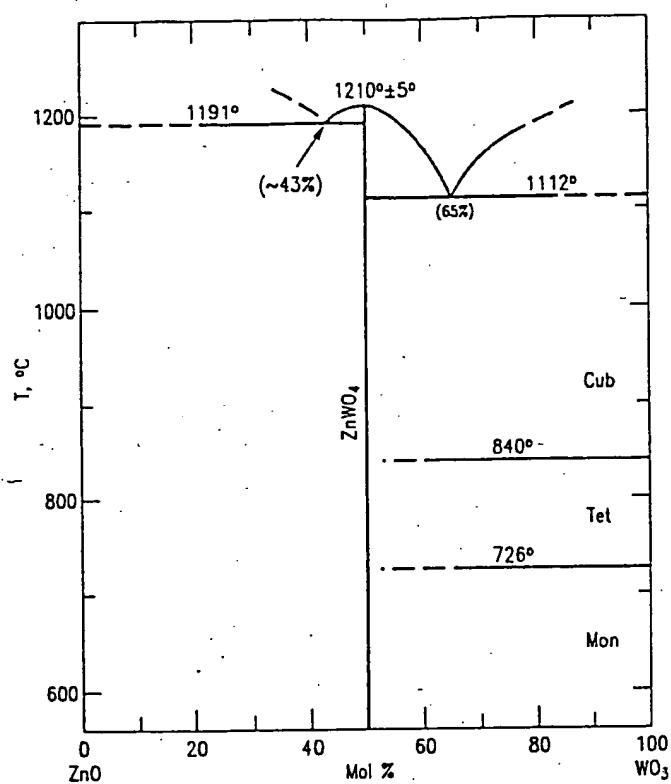
ZnO-WO₃

Fig. 9261—System ZnO-WO₃. Mon = monoclinic; Tet = tetragonal; Cub = cubic.

A. V. Shchenev, Yu. F. Kargin, and V. M. Skorikov, *Zh. Neorg. Khim.*, **33** [8] 2165-2167 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)*, **33** [8] 1237-1238 (1988).

The ZnO-WO₃ system was studied by X-ray diffraction, differential thermal analysis, and chemical phase analysis in the concentration range 10-85 mol% WO₃. The starting materials were highly-pure (for optical glass preparation) grade tungsten(VI) oxide and highly-pure grade zinc oxide. Approximately 12 specimens were prepared at 5-10 mol% intervals. Weighed specimens of the oxides were mixed, ground, and subjected to heating in stages with regrinding at each stage. (No mention was made about contamination.) The temperature was increased from 600°C to (0.9-0.95)T_{fusion}; the total heating time was about 120 h, and in some cases up to 200 h. X-ray diffraction confirmed that the reaction was complete. The thermal analysis was carried out on a DTA apparatus at heating and cooling rates of about 7°C min⁻¹ using platinum crucibles and previously-heated alumina as standard. The X-ray diffraction was carried out on a diffractometer (CuK α radiation, Ni-filter). Tungsten(VI) oxide in the specimens was determined gravimetrically, and zinc oxide by complexometric titration. The only compound formed in this system was normal zinc tungstate ZnWO₄, with melting point 1210° ± 5°C. Zinc tungstate formed eutectics with the original components: on the tungsten(VI) oxide side at 65 mol% WO₃ and 35 mol% ZnO with melting point 1122°C. The eutectic on the zinc oxide side with composition ~43 mol% WO₃ and 57 mol% ZnO corresponded to a eutectic line which could be followed in the range 52-85 mol% ZnO. The more accurate determination of the composition of this eutectic and the position of the liquidus line was made difficult by the

sublimation of the components at high temperatures. See Figs. 6433 and 9260 for earlier work.

S.K.S.

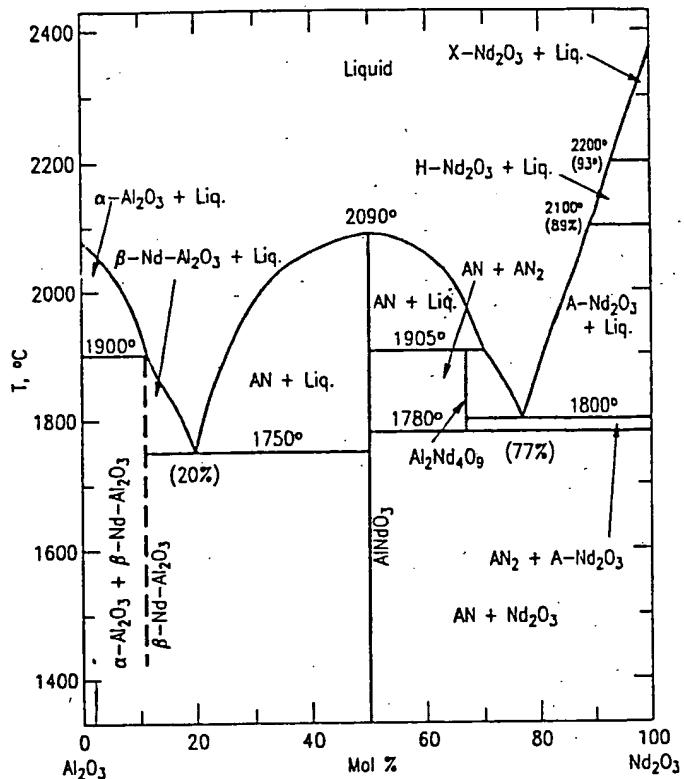
Al₂O₃-Nd₂O₃

Fig. 9262—System Al₂O₃-Nd₂O₃. AN = AlNdO₃; AN₂ = Al₂Nd₄O₉; A, H, and X = rare-earth oxide polymorphic forms; A and H are hexagonal; X is cubic; α -Al₂O₃ = corundum type; β -Nd-Al₂O₃ = NdAl₁₁O₁₈.

J. P. Coutures, *J. Am. Ceram. Soc.*, **68** [3] 105-107 (1985).

The tentative phase diagram for the system Al₂O₃-Nd₂O₃ is presented. The author pointed out the discrepancies in the previous studies.¹⁻⁴ The purities of Nd₂O₃ and Al₂O₃ used were 99.9% and 99.99%, respectively. Prior to use, Nd₂O₃ was annealed at 1200°C for 5 h in order to remove anionic impurities. The samples were prepared in air by co-melting ~30 mixtures of the starting oxides in a laboratory-scale solar furnace. Phase identification was done by room-temperature XRD (Ni-filtered CuK α radiation; goniometer scanning speed 1°C/min in 20). The liquidus and solidus lines were drawn from the results obtained by a thermal analyzer associated with a 2 kW horizontal-axis solar furnace. The temperatures were measured with an optical pyrometer under good blackbody conditions (λ pyrometer, 0.65 μm; practical emissivity, 0.99; calibration points, Al₂O₃ melting point 2053°C and Y₂O₃ melting point 2440°C). The temperature measurements expressed in the 68 IPTS are at ±10°C. The thermal analyses were performed for each composition under a 2 L/min flow of argon (~100 ppm O₂) or oxygen (99.9%). The system was scanned over the 0 to 100 mol% Al₂O₃ composition range in 5 mol% steps except between 10 and 35 mol% Al₂O₃ and between 70 and 100

Al₂O₃-Nd₂O₃ (concl.)

mol% Al₂O₃ where 2.5 mol% steps were used. Three compounds, a β -Al₂O₃-type compound, the perovskite NdAlO₃, and Nd₄Al₂O₉, were identified. The exact composition (or composition range) of the β -Nd-Al₂O₃ phase is not discussed. The perovskite melts congruently at 2090°C; and the other compounds exhibit incongruent melting behavior: β -Nd-Al₂O₃ at 1900°C and Nd₄Al₂O₉ at 1905°C. Nd₄Al₂O₉ decomposed below 1780°C into NdAlO₃ and A-Nd₂O₃. On the Nd₂O₃-rich side, and due to high temperature transitions (A-H at -2100°C and H-X at -2200°C) two metatectics are observed on the liquidus line at -2100°C, 11 mol%, and at -2200°C, 7 mol% Al₂O₃. The author observed for a given composition a depression of liquidus and solidus temperatures due to oxygen dissolution in the melt.

1. N. A. Toropov and T. P. Kiseleva, *Zh. Neorg. Khim.*, **6** [10] 2353-2358 (1961); *Russ. J. Inorg. Chem. (Engl. Transl.)*, **6** [10] 1193-1196 (1961).
2. M. Mizuno, T. Yamada, and T. Noguchi, *Yogyo Kyokasho*, **85** [2] 90-95 (1977).
3. E. Antic-Fidancev and P. Caro, *C. R. Séances Acad. Sci. Ser. C*, **284** [13] 471-474 (1977).
4. J. P. Coutures, E. Antic, and P. Caro, *Mater. Res. Bull.*, **11** [6] 699-706 (1976).

S.K.S.

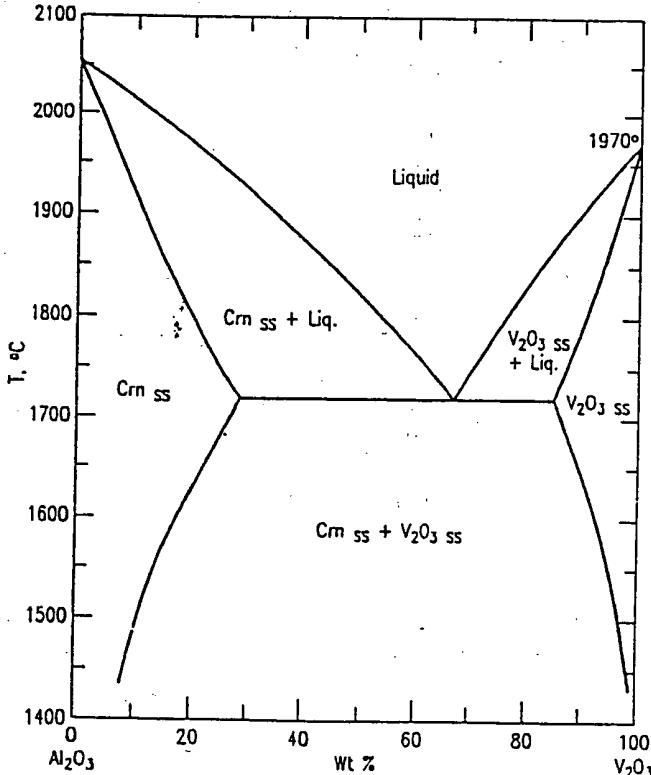
Al₂O₃-V₂O₃

Fig. 9263—System Al₂O₃-V₂O₃. Crn = corundum (Al₂O₃).

A. Muan and M. S. Najjar, "Compositions Involving V₂O₃-Al₂O₃-CaO", US Patent 5,070,065, 1991.

There are strong crystallographic similarities between V₂O₃ and other better known sesquioxides, such as Al₂O₃, Fe₂O₃, and Cr₂O₃. They all have the close-packed hexagonal corundum-type structure in which cations are in octahedral coordination. Among the trivalent cations forming these sesquioxides, Al³⁺ stands out as being considerably different from the others (Fe⁺³, Cr⁺³, and V⁺³). First, Al³⁺ is a noble gas-type ion. Second, it is significantly smaller than the other ions and, hence, can occur fairly readily in four-fold (tetrahedral), as well as six-fold (octahedral), coordination.

There is a lack of complete solid solubility between Al₂O₃ and V₂O₃. Corundum solid solution and V₂O₃ solid solution coexist with a liquid phase along the liquidus surface of the system.

See Figs. 9221 and 9259 for a discussion of experimental methods.

M.S.N.

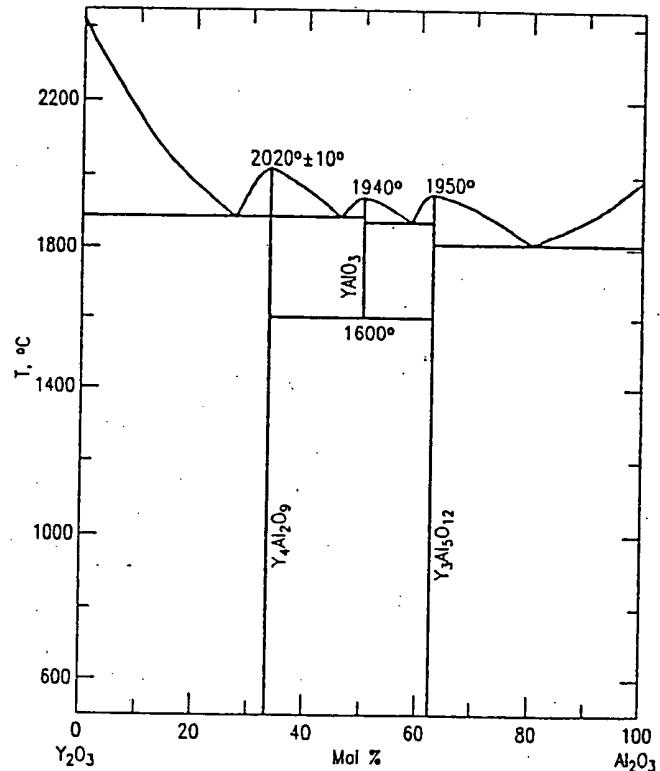
Al₂O₃-Y₂O₃

Fig. 9264—System Y₂O₃-Al₂O₃.

I. A. Bondar, L. N. Koroleva, and E. T. Bezruk, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **20** [2] 257-261 (1984); *Inorg. Mater. (Engl. Transl.)*, **20** [2] 214-218 (1984).

The starting materials were Y₂O₃ and Al₂O₃. Approximately 20 compositions were obtained by solid-phase synthesis by precipitation from nitrates and from the melt. Microscopy, X-ray diffraction, and X-ray spectral analysis were used to analyze products.

See Figs. 311, 312, 2344, and 4370 for earlier studies.

G.L.G.